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Air Pollution Assessment of Ethylene Dibromide

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Air Pollution Assessment of Ethylene Dibromide

R. JOHNS

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16. ABSTRACT Ethylene dibromide, a colorless, nonflammable hydrocarbon, is primarily employed as an additive in leaded gasoline to scavenge lead oxide residues from the combustion chambers of gasoline engines. Atmospheric measurements made near major suspected emission sources (service stations, refineries, production facilities) reveal ethylene dibromide concentrations several orders of magnitude below the threshold limit value of 25 ppm established by the American conference of Governmental Industrial Hygienists. Ethylene dibromide generally acts as a central nervous system depressant, although it is not as effective as many of the other halohydrocarbons. In cases of death, pneumonia is normally the cause due to lung damange induced by the chemical. Symptoms of acute exposure include lung inflammation, congestion, edema, and hemorrhaging. A significant environmental hazard does not appear to be present in regard to ethylene dibromide; however, due to the lack of available data documenting long term, low level exposure in humans the compound cannot be considered environmentally innocuous.

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ABSTRACT

Ethylene dibromide, a colorless, nonflammable hydrocarbon, is primarily employed as an additive in leaded gasoline to scavenge lead oxide residues from the combustion chambers of gasoline engines. In the course of this application, the compound is combusted and the bromine component of the compound is released to the atmosphere via the automobile exhaust. Atmospheric measurements made near major suspected emission sources (service stations, refineries, production facilities) reveal ethylene dibromide concentrations several orders of magnitude below the threshold limit value of 25 ppm established by the American Conference of Governmental Industrial Hygienists. Although the halohydrocarbon has been environmentally detected, it does degrade slowly in the atmospheric and aquatic receiving environments with estimated respective half-lives of 100 days and 5 to 10 days. Therefore, no appreciable environmental accumulation would be expected.

Ethylene dibromide generally acts as a central nervous system depressant, although it is not as effective as many of the other halohydrocarbons. In cases of death, pneumonia is normally the cause due to lung damage induced by the chemical. Symptoms of acute exposure include lung inflammation, congestion, edema, and hemorrhaging.

A significant environmental hazard does not appear to be present in regard to ethylene dibromide; however, due to the lack of available data documenting long term, low level exposure in humans the compound cannot be considered environmentally innocuous.

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I. SUMMARY AND CONCLUSIONS

Ethylene dibromide is a colorless, nonflammable liquid of high density and chloroform-like odor. It is a good solvent for resins, gums, waxes, and many organic chemicals, but its major use is as an additive in leaded gasoline. The compound is miscible with benzene, carbon tetrachloride, ether, alcohols, and many other solvents. The low vapor pressure and appreciable water solubility of the compound tend to promote environmental persistence in water and soil as well as in the atmosphere.

Ethylene dibromide is inert at ordinary temperatures, but is hydrolyzed to ethylene glycol and bromoethanol when heated with water. The compound shows a half-life at 5 to 10 days toward hydrolysis under neutral conditions at ambient temperature. This would tend to promote limited persistence in the aquatic environment. Ethylene dibromide is resistant to atmospheric oxidation by peroxides and ozone, typically showing half-lives in excess of 100 days toward these reactions. The terminal halogen atoms of the molecule are moderately reactive in synthesis, making the compound useful as an intermediate in the production of other chemicals. It is the least expensive organic bromine compound available.

Ethylene dibromide is readily absorbed through the lungs, skin and gastrointestinal tract of mammals. It is excreted unchanged by the lungs and is partially decomposed in the body, producing bromide

residue in the urine. Pathological effects of the chemical are found primarily in the liver, lungs, and kidneys of mammals.

Acute human toxicity of ethylene dibromide vapor is documented primarily from accidents. The compound was mistaken for ethyl bromide and administered as an anesthetic during earlier stages of development of anesthesiology. Quantities up to 100 grams were administered under these circumstances, resulting in irritation of the larynx, conjunctivae, and lungs. Patients became weak, nervous, pale, suffered vomiting and diarrhea, and died from circulatory failure within 24 to 48 hours. Acute exposure of dogs to 50,000 mg/m^3 vapor concentration for 15 to 45 minutes results in vomiting and convulsions, cloudiness of the cornea, and death within 24 hours. Mice survive a concentration of 10,000 mg/m^3 for 30 minutes but die from a 60-minute exposure at this level. Guinea pigs survive a seven-hour exposure to 1,536 mg/m^3 ethylene dibromide vapor but a similar exposure to 31,000 mg/m^3 is fatal. A significant toxicity characteristic of ethylene dibromide is the relatively narrow margin between recoverable and fatal exposures to the vapor.

Chronic exposure to ethylene dibromide vapor at concentrations significantly above the threshold limit value (190 mg/m^3) can produce symptoms similar to those of acute exposure. These effects have been demonstrated using test animals as subjects. Rats exposed for six months (35 hours/week) to 385 mg/m^3 suffered 50 percent mortality from pneumonia and respiratory infection, the survivors

showing weight increases in lungs, liver and kidneys. Guinea pigs subjected to 57 seven-hour exposures in 80 days (385 mg/m^3 vapor concentration) showed reduced weight but normal mortality. Among rats, rabbits and guinea pigs, rats showed the greatest respiratory sensitivity to the chemical. Chronic vapor exposure results in pathological damage to lungs, liver, kidneys and spleen of most species.

Ethylene dibromide may be absorbed through the skin in sufficient amounts to cause fatal poisoning. Rabbits died within four days from the application of 1.0 g/kg-body-weight to shaved skin for 24 hours. Skin absorption is a significant concern in the industrial environment, where workers' shoes may be splashed with the chemical.

Acute oral toxicity of ethylene dibromide in humans is documented from the ingestion of 4.5 ml of the chemical in a suicide. Symptoms of prolonged vomiting, diarrhea and anuria were followed by death in 54 hours. Autopsy revealed massive liver and kidney damage. Oral toxicity studies in animals reveal LD_{50} values ranging from 0.055 g/kg-body weight in female rabbits to 0.420 g/kg-body weight in female mice. Chronic oral doses of ethylene dibromide have been shown to produce stomach cancer in mice and rats. When administered chronically at one-half the maximum tolerated dose, the compound induced a high incidence of squamous cell carcinoma of the stomach in these animals within 10 weeks.

Ethylene dibromide has been demonstrated to distinctly mutagenic toward Salmonella typhemurium and Serratia marcescens by host-mediated assay techniques in mice. The teratogenicity of the compound has not been reported. Dietary concentrations of 5 to 40 mg/kg in feed cause reductions in weight and fertility of eggs produced by laying hens. This finding is significant in that the chemical is used for fumigation of feed grains. Repeated oral doses of ethylene dibromide are found to cause malformations of the sperm in bulls when administered at a level of 4 mg/kg-body-weight on alternate days for three weeks.

In the aquatic environment, sunfish and largemouth bass show median 24-hour tolerance limits of 15 to 50 mg/kg ethylene dibromide in river waters. Within this range, the results are influenced by the source of the natural water sample.

Ethylene dibromide vapor is monitored in the industrial environment for compliance with Occupational Safety and Health (OSHA) regulations, which limit workplace atmospheres to 155 mg/m^3 (20 ppm) for eight-hour-average daily exposures. Measurements in the open atmosphere are sparse. The Environmental Protection Agency (EPA) has recently reported levels of 0.069 to 0.110 $\mu g/m^3$ along urban roadways in three western cities. Population exposure at the maximum level is such that 1,400 years would be required to accumulate the occupational dose from a single day's work at the OSHA limit. Therefore, these measurements indicate no risk to the exposed population. Maxium levels of 90 to 115 $\mu g/m^3$ were found on the premises

of ethylene dibromide production facilities as a part of the same study. These data were employed in a crude diffusion model, along with hypothetical plant parameters, to predict downwind atmospheric concentrations to which neighboring populations might be exposed. A level of about 6 g/m^3 was predicted for a point 500 meters downwind of one facility, assuming a wind velocity of 6 m/sec. An exposure of 23 years to this concentration of ethylene dibromide is equivalent in dose to an eight-hour day at the maximum legal workplace concentration.

Potential exposure risks may stem from the use of ethylene dibromide as a fumigant for soil and grain, a highly dispersive application which is inherently difficult to control. Fumigation of storage structures that are normally enclosed may expose workers or any individuals in the vicinity to excessive levels of the airborne chemical. Exposure is possible in the distribution network of gasoline since the material is employed as an additive in automobile fuel.

Ethylene dibromide is readily analyzed in air by gas chromatography, using an electron capture detector. This detector is selective toward halohydrocarbons and effective in attenuating background response from other chemicals. A semi-quantitative test for ethylene dibromide vapor may be made with the halide lamp detector, a simple instrument which is specific for organic halogen compounds and responds to ethylene dibromide at levels above 380 mg/m^3 (50 ppm).

Domestic production of ethylene dibromide totaled 331 million pounds in 1973. The chemical is produced at six domestic facilities which are clustered in the Gulf Coast region of the United States. The chemical has shown an annual production growth of 3 to 5 percent during the last decade, but future growth is uncertain. Ethylene dibromide is used as an additive in leaded motor fuel, and this use accounts for 85 percent of consumption. Production can be expected to fall toward 15 percent of its projected current level once the use of leaded gasoline is abandoned. Among other uses, about five percent of ethylene dibromide consumption is used in the synthesis of other organic chemicals and 10 percent is used dispersively as a solvent and fumigant. It is an ingredient in many commercial insecticides, but is not otherwise sold as a commercial product. There are no known natural sources of the chemical.

As a fuel additive, ethylene dibromide serves to scavenge lead oxide residues from combustion chambers of gasoline engines through conversion of the oxide to volatile lead bromide. While ethylene dibromide undergoes combustion with the fuel, the bromine content of the compound is emitted to the atmosphere as engine exhaust. A major fraction of all bromine produced ultimately reaches the atmosphere in this form.

Ethylene dibromide does not appear to be a substance with significant environmental hazards. However, since little information is available to assess potential long-term low level effects or

possible synergistic effects, the chemical cannot be considered environmentally safe. Preliminary measurements of airborne ethylene dibromide near major sources of suspected emissions (service stations, highways, refineries, and production facilities) show levels of ethylene dibromide which are several orders of magnitude below the threshold limit value. Furthermore, it shows a reasonable tendency to degrade in both atmospheric and aquatic receiving environments with estimated half-lives of 100 days and 5 to 10 days, respectively. No net environmental accumulation is suspected.

Major emission sources of ethylene dibromide which may be potential hazards are its dispersive uses in agriculture. It is employed as a fumigant for soil and grain and as an ingredient in insecticides. As such, it has been demonstrated to affect growth and behavior patterns of several agricultural species. Residues of the material have also been measured in some food products of exposed agricultural produce.

It is recommended that ambient concentrations of ethylene dibromide be measured near dispersal facilities to determine if harmful quantities of the material are reaching all receiving environments (air, water, soil). This would allow evaluation of the acceptability of the material for these uses. If unacceptable levels are measured, either substitute materials or improved dispersal techniques should be developed.

A study should be conducted to determine the extent and levels to which ethylene dibromide occurs in food products. If significant results are obtained, studies should be conducted to explore the effect these levels of ethylene dibromide may have on populations consuming these foodstuffs.

II. AIR POLLUTION ASSESSMENT REPORT

A. PHYSICAL AND CHEMICAL PROPERTIES

Ethylene dibromide is a dense, colorless, nonflammable liquid resembling chloroform in odor, and possessing good solvent properties for resins, gums, waxes and other organic compound (1). The principal physical properties of the compound are shown in Table I. The low vapor pressure and appreciable water solubility of ethylene dibromide would tend to promote environmental persistence in water and soil in cases of liquid spills. The bromohydrocarbons are much less volatile than their chlorine analogs, and ethylene dibromide solidifies at about 10°C. It is fully miscible with benzene, carbon tetrachloride, ether, anhydrous alcohols and many other solvents.

The compound is generally inert at normal temperatures, although slight decomposition may result from exposure to light (1). It is hydrolyzed to ethylene glycol and bromoethanol at elevated temperature. When heated to 340 to 370°C, ethylene dibromide decomposes into vinyl bromide and hydrobromic acid. The terminal halogen atoms are reactive, making the compound a useful synthetic intermediate. It is the least expensive organic bromine compound available.

Ethylene dibromide is resistant to atmospheric oxidation by peroxides and ozone, typically showing half-lives toward these reactions of 100 days or more (2). The compound is generally less reactive in the atmosphere than corresponding alkanes or olefins.

TABLE I
ETHYLENE DIBROMIDE

Physical Properties	
Chemical Formula	$BrCH_2-CH_2Br$
Molecular Weight	187.88
Boiling Point	131.6°C
Melting Point	9.97°C
Vapor Pressure, 25°C	12 mm
Specific Gravity, liquid	2.17
Specific Gravity, vapor, 25°C	6.5
Refractive Index 20°C	1.5379
Solubility, water, 20°	4.3 g/l
Solubility, Octanol	∞
Conversion Factors	1 mg/l 247 ppm
@ 25°C/760 mm Hg	1 ppm 4.05 mg/m^3

Source: Kirk, R. E., Encyclopedia of Chemical Technology, Second Edition, Vol. 3, p. 771, New York, Wiley, 1968.

Ethylene dibromide is hydrolyzed in water, having a half-life of 5 to 10 days toward this reaction; the reaction is favored by acid conditions (2). Because of the paucity of data, it is impossible to assess environmental accumulation of the chemical, but rates of atmospheric degradation may be sufficient to handle the environmental burden adequately.

B. EFFECTS

Ethylene dibromide is readily absorbed through the lungs, from skin contact, and through the gastrointestinal tract of mammals (3, 4). The chemical shows a mild tendency for accumulation in brain and liver tissue, as shown by experiments with laboratory animals (4). It is excreted unchanged by the lungs and is partially decomposed in the body, producing bromide residue in the urine.

This chemical acts as a depressant to the central nervous system in mammals, although it is relatively weaker in this effect than other halohydrocarbons. Acute vapor exposure typically results in lung inflammation, congestion, edema and hemorrhaging (3). Liver damage is evidenced as cloudy swelling, fatty degeneration and necrosis; whereas, the kidneys show slight interstitial congestion and edema. Deaths from acute exposure at high vapor concentrations are usually due to pneumonia, developed as a result of lung injury (4). Acute human toxicity of ethylene dibromide vapor is documented primarily from accidents. At the turn of the century, the compound was occasionally confused with ethyl bromide, and erroneously administered, and resulted in irritation of the larynx, conjunctivae, and lungs. Patients became weak, nervous, pale, suffered vomiting and diarrhea, and died from circulatory failure within 24 to 48 hours.

Animal studies have provided additional information on the acute vapor toxicity of ethylene dibromide. Exposure of dogs to

50,000 mg/m^3 vapor concentration for 15 to 45 minutes resulting in vomiting and convulsions, cloudiness of the cornea, and death within 24 hours (6). Selected data on the acute toxicity of ethylene dibromide to laboratory animals are shown in Table II. A significant toxicity characteristic of ethylene dibromide is the relatively narrow margin between recoverable and fatal exposures to the vapor. This is demonstrated by experiments with mice, in which the animals survived 10,000 mg/m^3 vapor concentration for 30 minutes without permanent damage, but died within 5 hours from a 60-minute exposure at the same concentration (7).

Chronic exposure to ethylene dibromide vapor at concentrations significantly above the threshold limit value (TLV)* can produce symptoms similar to those of acute exposure. The threshold limit has been established at 190 mg/m^3 (25 ppm) by the American Conference of Governmental Industrial Hygenists (9). Because there is a narrow margin between tolerable vapor concentrations of ethylene dibromide and those causing severe injury, the threshold limit must be scrupulously observed. Worker exposure is limited under Occupational Safety and Health regulations to an 8-hour-average concentration of 155 mg/m^3 (20 ppm) (10).

The effects of chronic vapor exposure have also been demonstrated using laboratory animals. Most species exposed to ethylene dibromide

*Airborne concentration which induces no physiological response after repeated exposure.

TABLE II
ACUTE TOXICITY OF ETHYLENE DIBROMIDE

Animal	Route	Dose	Dosage	Exposure	Reference
Mouse	Inhalational	LC_0	10,000 mg/m^3	30 minutes	6
Mouse	Inhalational	LC_{100}	42,000 mg/m^3	3 minutes	6
Mouse	Inhalational	LC_{100}	10,000 mg/m^3	1 hour	6
Mouse (female)	Oral	LC_{50}	0.420 g/kg-body wt.		3
Rat (male)	Oral	LC_{50}	0.146 g/kg-body-wt.		3
Rat (female)	Oral	LC_{50}	0.117 g/kg-body wt.		3
Guinea pig	Inhalational	LC_0	1,536 mg/m^3	7 hours	5
Guinea pig	Inhalational	LC_0	3,074 mg/m^3	2 hours	5
Guinea pig	Inhalational	LC_{100}	31,000 mg/m^3	6-18 hours	7
Guinea pig	Oral	LD_{50}	0.110 g/kg-body-wt.		3
Rabbit	Epidermal	LD_{40}	0.30 g/kg-body-wt.	24 hours	3
Rabbit	Epidermal	LD_{100}	1.1 g/kg-body-wt.	24 hours	3
Rabbit (female)	Oral	LD_{50}	0.055 g/kg-body-wt.		3
Dog	Inhalational	LD_{100}	50,000 mg/m^3	15-45 minutes	6

LC_0--Survivable Concentration (concentration lethal to none of a sample population under stated experimental conditions).

LC_{100}--Lethal Concentration (concentration lethal to 100 percent of a sample under stated experimental conditions).

LD_{50}--Dose lethal to 50 percent of a sample population under stated experimental conditions.

LD_{100}--Dose lethal to 100 percent of a sample population under stated experimental conditions.

vapor showed damage to lungs, liver, kidneys, and spleen (3). In an extensive study, Rowe et al. (3) exposed various animals to vapor concentrations of 190, 385, and 770 mg/m^3 of ethylene dibromide on a schedule of 7 hours/day, 5 days/week for periods up to six months. Rats and rabbits exposed to 770 mg/m^3 concentration in this study showed loss of weight, physical degeneration, and some deaths within the first ten days of exposure. Rats exposed to 385 mg/m^3 vapor concentration showed 50 percent mortality from pneumonia and respiratory infection, but the survivors lived through the six-month exposure. These survivors showed weight increases in lungs, liver and kidneys, and histopathological changes in the lungs. Guinea pigs subjected to 57 7-hour exposures in 80 days (385 mg/m^3 vapor concentration) showed reduced weight but normal mortality (3). A vapor concentration of 190 mg/m^3 (the threshold limit value) was well tolerated by rats, guinea pigs, rabbits and monkeys. Rats showed the greatest respiratory sensitivity among this group of animals. Kochmann has described the overt symptoms of chronic vapor exposure in cats and rabbits as sneezing, marked salivation, tremors and incoordination (7).

A study, conducted by R. D. Short et al. of the Midwest Research Institute for the Environmental Protection Agency evaluated the developmental toxicity of ethylene dibromide in rats and mice during organogenesis. The experimental animals were bred and subsequently exposed to atmospheric concentrations of 30 ppm ethylene dibromide

for 23 hours each day during days 6 to 16 of the gestation period. No significant mortality was observed in the adults exposed to the compound; however, rat litter size was decreased and hydrocephaly and minor costal anomalies were observed in the fetuses from the exposed rats (8).

Ethylene dibromide may be absorbed through the skin in sufficient amounts to cause fatal poisoning (11). Rabbits died within four days as a result of the application of 1 g/kg body weight to shaved skin for 24 hours (3). Skin absorption is a significant concern in industry, particularly when workers' shoes may be splashed with the chemical. Application of the undiluted chemical to the eye of rabbits causes severe conjunctival irritation and very slight superficial necrosis over a period of 48 hours (3).

Acute oral toxicity of ethylene dibromide in humans is documented by a single case in which 4.5 ml of the liquid chemical was ingested in a suicide (12). Ingestion was followed immediately by prolonged vomiting and later by diarrhea, then anuria* and death 54 hours after poisoning. Autopsy revealed massive centrilobular necrosis of the liver and proximal kidney damage (12). Acute oral toxicity of the compound to laboratory animals is shown in Table II.

Chronic oral doses of ethylene dibromide have been shown to produce stomach cancer in mice and rats (13). When administered

*Anuria - suppression or absence of urine.

chronically at one-half the maximum tolerated dose, the compound induced a high incidence of squamous cell carcinoma of the stomach within 10 weeks. Various quantities of ethylene dibromide resulted in carcinomas in 76 percent of rats and 87 percent of mice (10).

Ethylene dibromide has been demonstrated to be distinctly mutagenic in host-mediated assay in mice at a level of 500 mg/kg serum concentration; back-mutations were detected using intraperitoneal-injected suspensions of histidine-requiring Salmonella typhimurium and leucine-requiring Serratia marcescens as mutants (14). Ethylene dibromide showed no definite mutagenicity in a dominant lethal test in mice (14).

Bulls have been found to be subject to sperm malformation as a result of oral doses of ethylene dibromide of 4 mg/kg body weight administered on alternate days for 3 weeks (15,16). Malformations appeared about two weeks after the first dose and included total disintegration of sperm cells. Similar results were obtained when 120 mg of the compound was injected into the fluid surrounding each testes of bulls. The significance of the oral study stems from the general use of ethylene dibromide as a fumigant for grain.

The effects of dietary ethylene dibromide on the growth of chicks and on the egg production of laying hens have been studied (17,18). Chicks fed a diet containing 40 mg/kg concentration of the compound showed reduced weight gains, reduced food consumption and reduced feed efficiency. Kidney and liver tissues were found to

contain bromides. Egg weights of laying hens were reduced significantly by the presence of residual ethylene dibromide in their diet of oats (18). Levels as low as 5 mg/kg in feed were found to be toxic. Another study confirmed that ethylene dibromide was responsible for reduction in the weight of hens' eggs, and that eggs from some hens fed unspecified amounts of ethylene dibromide were infertile (19). These studies underline the need for caution in the use of the chemical as a fumigant for feed grains. Fumigation with ethylene dibromide has also been shown to affect adversely the germination rate of seeds, particularly under conditions of high humidity and temperature (20).

The toxicity of ethylene dibromide in the aquatic environment has been studied using bluegill sunfish and largemouth bass as subjects (21). The fish, of fingerling size, were exposed to various concentrations of the chemical in river water matrices. Sunfish showed median tolerance limits of 15 to 18 mg/kg concentration, whereas bass showed median limits of 25 to 50 mg/kg under similar experimental conditions. The experimental results were found to be somewhat dependent on the source of the river water (21).

C. AMBIENT CONCENTRATIONS, POPULATION AT RISK AND MEASUREMENT TECHNOLOGY

Ethylene dibromide is controlled in industrial atmospheres for purposes of occupational safety. Measurements of this chemical in the ambient atmosphere are rare. A threshold limit value of 190 mg/m^3 (25 ppm) vapor concentration has been established by The American Conference of Governmental Industrial Hygenists. Occupational Safety and Health regulations limit industrial atmospheres to 155 mg/m^3 (20 ppm) as an 8-hour average for daily exposures of workers (3). Compliance data are not readily available, but industrial levels are claimed to be maintained well below this limit.

The principal population exposure from ethylene dibromide arises from dispersive uses of the chemical. The compound is used as an additive in leaded gasoline, and this use accounts for 85 percent of commercial demand. This application is not truly dispersive since the compound ultimately undergoes combustion with the fuel, yet ethylene dibromide may be lost to the environment throughout the extensive production and distribution chain which serves the gasoline market. The population risk from this source should be small, considering the low vapor pressure of ethylene dibromide and its concentration of about 0.05 percent by volume in fuel.

Preliminary measurements of atmospheric ethylene dibromide at selected locations have recently been reported by the Environmental Protection Agency (4). Sites were chosen near sources of the chemical which are generally related to gasoline production, distribution and use. Urban locations near arterial streets in three Western cities

were chosen to represent worst-case ambient levels of ethylene dibromide. These sites were located near roadways carrying traffic loads of 25,000-50,000 vehicles per day, and each site was within 200-300 feet of two or more gasoline service stations. The sampling probes were directed into the wind in each case and positioned 6 feet from the ground. The results of the urban study are presented below.

ATMOSPHERIC CONCENTRATION OF ETHYLENE DIBROMIDE

Urban Roadway Sites

City	Concentration, $\mu g/m^3$
Phoenix, Arizona	0.069
Los Angeles, California	0.11
Seattle, Washington	0.083

The observed concentrations are reasonably uniform between the cities, considering the many variables involved, and are about six orders of magnitude below the threshold limit value. An exposure of about 1,400 years at a typical urban roadway site would be required to accumulate the dose a worker receives at the OSHA limit in one working day.

The atmospheric concentration of ethylene dibromide was also measured at two locations on the premises of an oil refinery as a part of the same study (4). Atmospheric levels ranged from 0.23 to 1.65 $\mu g/m^3$ at locations 50-400 feet downwind of bulk transfer and tank truck loading operations. While these concentrations range up to

tenfold larger than urban roadway levels, they are still several orders of magnitude below levels considered hazardous. More than 100 years' exposure on the premises of an oil refinery would be required to accumulate the occupational dose from a single day's work at the maximum legal concentration.

Atmospheric levels of ethylene dibromide were also measured at production facilities of two major manufacturers of the chemical (22). Maximum levels of 90-115 $\mu g/m^3$ were recorded at downwind locations near the perimeters of these properties, as detailed in Table III. While these levels are significantly larger than those observed at roadway or refinery sites, a calculation shows that a 17-month exposure, at a representative level of 100 $\mu g/m^3$, would be required to equal the occupational dose from a single 8-hour day at the OSHA limit of 155 mg/m^3.

The atmospheric concentrations of ethylene dibromide at production facilities may be used in a Gaussian plume equation*

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*Ground level downwind concentrations resulting from a point source are predicted by the following equation:

$$\chi(x, 0, 0; H) = \frac{Q}{\pi \sigma_y \sigma_z u} \exp \left[-1/2 \left(\frac{H}{\sigma_z} \right)^2 \right]$$

where: Q = uniform emission rate (grams/sec)
u = mean wind speed affecting the plume (meters/sec)
H = effective stack height, that is sum of stack height plus plume rise (meters)
σ_y = horizontal dispersion coefficient evaluated in terms of downwind distance to the point for which the contration is being computed (meters)
σ_z = vertical dispersion coefficient evaluated in terms of downwind distance to the point for which the concentration is being computed (meters)
χ = ground level concentration on plume axis (grams/meter^3)

TABLE III
ATMOSPHERIC LEVELS–ETHYLENE DIBROMIDE PRODUCTION PLANTS

Facility	Maximum Level**	Emission Rate	Estimated Level*
Dow Chemical Magnolia, AR	115 $\mu g/m^3$, 76 m downwind	0.00862 g/sec	6.26 $\mu g/m^3$
Ethyl Corporation Magnolia, AR	90 $\mu g/m^3$ 30 m distant 45° from downwind	5.097 g/sec	356 $\mu g/m^3$

Source: U.S. Environmental Protection Agency. "Sampling and Analysis of Selected Toxic Substances. Task II--Ethylene Dibromide." Final Report, September, 1975, EPA 560/6-75-001.

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*Estimated level 500 m downwind, wind at 6 m/sec.

according to Turner (23) to predict downwind atmospheric levels of the chemical in surrounding neighborhoods. The basic diffusion equation must be modified, however, due to the effect of the plant itself on the flow of air. Mechanical turbulence in the wake of a building tends to produce aerodynamic downwash, resulting in the fairly rapid diffusion of a gaseous emission down to the ground. This region of disturbed flow extends downwind a distance equal to several times the height of the building. While this situation does not result in a Gaussian distributed plume, it is proposed that a modification of the usual formula still can be employed. This is because the turbulent mixing in the wake of the building is assumed to be distributed uniformly in the vertical direction, analogous to the situation wherein a plume is trapped below an inversion layer. A limited vertical mixing height can be modeled using the equation:

$$\chi(x,0,z;\ H) = \frac{Q}{\pi\sigma_y u\ (.8L)}$$

where L is the limit of the mixing depth. In the case of an isolated rectangular building it is assumed that L equals 1.5 times the building height.

In addition there is a horizontal wind turbulence which is assumed to result in an initial horizontal plume spread equal to the width of the building normal to the wind direction. This is analogous to an area source emission with the area equal to the building top. This can be modeled using a further modification of the basic Gaussian diffusion equation.

A virtual point source is assumed upwind of the building at a distance where the plume spread (for the given stability conditions) would equal the crosswind width of the building. The modified diffusion equation is, therefore:

$$\chi(x,0,z;\ H) = \frac{Q}{\pi\sigma'_y u(1.2h)}$$

where h is the building height and σ'_y is based on the downwind distance to the receptor point, plus the upwind distance to the virtual point source.

The measured atmospheric levels of ethylene dibromide at the two production facilities were used in the foregoing equation to determine mass emission rates, Q, from the two plants. These rates were then used in the diffusion equation to estimate concentrations at points 500 m downwind of the plants under an assumed wind velocity of 6 m/sec. The results are shown in Table III. Acute toxicity of ethylene dibromide levels near the two facilities are seen to differ by about fifty fold, a rather surprising range. The downwind concentration estimate for the Dow facility is considered the more credible value since it is based on a chemical measurement at a point directly downwind of the plant. Population exposure to this concentration of ethylene dibromide at a distance of 500 meters from the plant is such that a 23-year exposure would be equivalent in dose to an 8-hour working day at the maximum occupational level.

Limited measurements of ethylene dibromide in runoff water were made at two sampling sites as part of the aforementioned EPA study (4). Samples from an ethylene dibromide manufacturing facility and from the bulk loading area of a petroleum refinery showed similar concentrations of about 1 µg/l. The samples were taken from small streams within the respective premises. In one case, the runoff stream is directed to a biodegradation pond for further treatment.

Potential population risks may stem from the use of ethylene dibromide as fumigant for soil and grain. The chemical is used for the control of wire worms and nematodes in soil, and for insect control in grain storage facilities. While these applications account for a small fraction of ethylene dibromide consumption, they are totally dispersive, and offer paths to the soil as well as to the aquatic and atmospheric environment. Although no quantitative data are available, it can be envisioned that control of fumigant applications is difficult and they entail the risk of both occupational and residential exposure. Fumigation of grain storage structures may expose workers, bystanders and neighboring residents to excessive atmospheric concentrations of the chemical. Ethylene dibromide is also used industrially as a specialty solvent, but is not sold as a consumer product.

Ethylene dibromide, as other halohydrocarbons, is readily analyzed in air by means of gas chromatography using an electron

capture detector (24). This detector is selective toward organic halogen compounds and effective in attenuating background response from other chemicals. Other methods depend on oxidation or hydrolysis of ethylene dibromide and subsequent quantitative determination of inorganic bromide by conventional wet analysis. Such methods are more time-consuming than chromatography but are useful in laboratories that lack chromatographic equipment. Airborne ethylene dibromide responds to the halide lamp detector (Beilstein test). This simple and inexpensive detector is specific for organic halogen compounds, but does not distinguish among them. The halide lamp is in common use for the detection of fluorocarbon leaks from refrigeration systems, and provides a qualitative or semi-quantitative indication of the presence of halohydrocarbons at the detection level of the instrument, usually about 50 ppm or 380 mg/m^3 of ethylene dibromide.

D. SOURCES

Ethylene dibromide is a major industrial chemical by virtue of its use in leaded motor fuel, which accounts for 85 percent of demand. Domestic production of the chemical by direct combination of ethylene and bromine totaled 331 million pounds in 1973 (25). The chemical has shown strong long-term growth, which has leveled to an annual rate of 3 to 5 percent over the last decade (25). Production can be expected to fall toward 15 percent of its projected current level as leaded fuel approaches obsolescence. Ethylene dibromide is produced at six domestic facilities which are generally clustered in the Gulf Coast region, as shown in Figure 1; detailed plant locations are given in Table IV. The Gulf region is favored because its brine fields provide the bromine supply needed in the synthesis of ethylene dibromide. Furthermore, the complex of petroleum refineries in the region provides the major commercial market for the chemical.

The flow of ethylene dibromide in commerce is depicted in Figure 2. Foreign trade plays a minor role in the supply of this chemical. The data of Figure 2 indicate that about 36 million pounds of the chemical, or 11 percent of production, are released to the environment per year, exclusive of fuel losses, which are discussed below. There are no known natural sources of the chemical.

As a fuel additive, ethylene dibromide serves to scavenge lead oxide residues from combustion chambers of gasoline engines through conversion of the oxide to volatile lead bromide. Lead oxide residues

FIGURE 1
ETHYLENE DIBROMIDE PRODUCTION LOCATIONS

Source: Stanford Research Institute, Chemical Economics Handbook.

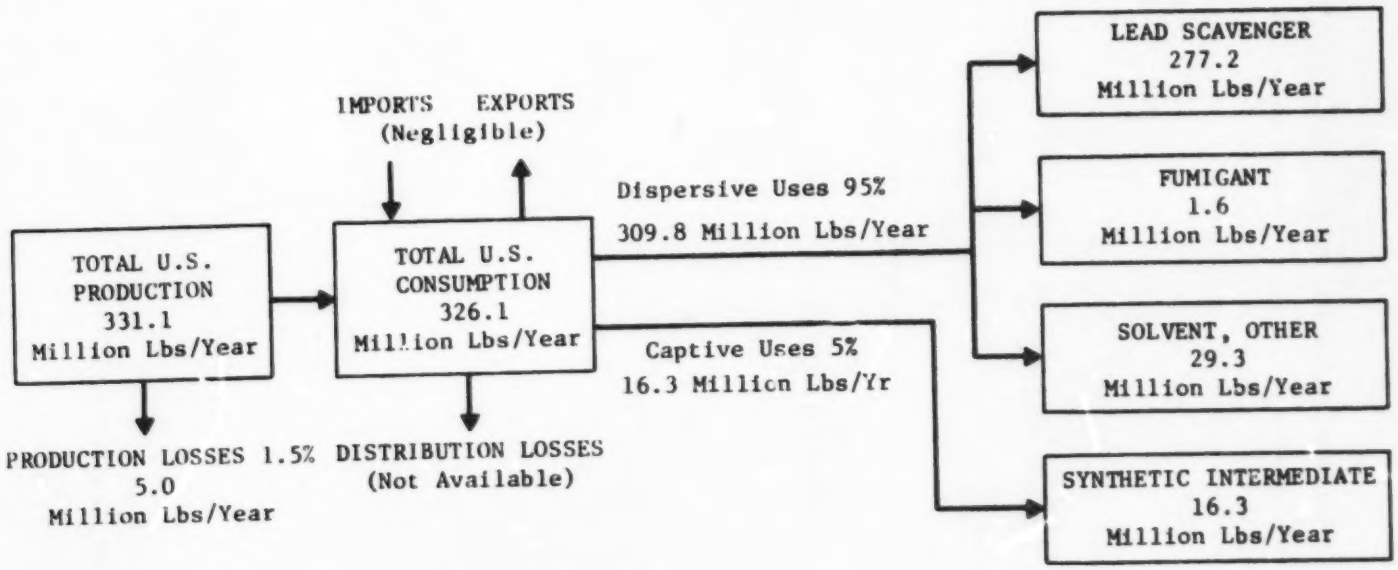
TABLE IV
ETHYLENE DIBROMIDE PRODUCTION LOCATIONS*

Company	Location
Dow Chemical, U.S.A.	Magnolia, Ark. Midland, Mich.
Ethyl Corporation	Magnolia, Ark.
Great Lakes Chemical Corporation	El Dorado, Ark.
Northwest Industries	El Dorado, Ark.
PPG Industries	Beaumont, Tex.

Source: Stanford Research Institute, Chemical Economics Handbook.

*Capacities not available.

FIGURE 2
ETHYLENE DIBROMIDE–COMMERCIAL PATHWAYS



results from the use of fuels containing tetraalkyl lead compounds as anti-knock agents. Since ethylene dibromide undergoes combustion with the fuel, this application is dispersive only with respect to losses which occur in the distribution and handling of gasoline. As a consequence of combustion, the bromine content of the chemical is released to the atmosphere as lead bromide through engine exhaust. A major fraction of all bromine produced reaches the atmosphere in this form. This is a declining problem, however, since ethylene dibromide will be eliminated from gasoline as the use of leaded fuel is abandoned.

Ethylene dibromide is a useful synthetic intermediate and the most widely used bromine compound available. It is used in the synthesis of dyes, pharmaceuticals and other organics, but these applications account for only 5 percent of demand. These uses are totally non-dispersive, and probably do not lead to formation of reaction products which pose significant problems as environmental contaminants.

The compound is also used as a fumigant for soil and grain, and as an ingredient in many commercial insecticides. These applications are highly dispersive and potentially hazardous from the standpoint of occupational and population exposure. Ethylene dibromide is used as a specialty solvent for resins, gums and waxes, but presumably under industrial conditions of controlled risk. The compound is not available as a consumer product.

E. CONTROL STRATEGY

Ethylene dibromide is a major industrial chemical whose use in motor fuel subjects the compound to broad distribution in the environment at low concentrations. Preliminary measurements of airborne ethylene dibromide near production facilities, refineries, and roadways, show levels which appear clearly free of population risk. The data indicate that no additional control is needed to restrict population exposure from these sources. Because of the low vapor pressure of the chemical and its small concentration in fuel (0.05%), hazardous local excesses are unlikely to occur in normal handling of gasoline. Fuel-related sources of ethylene dibromide are, moreover, in a position of diminishing importance, since this use of the chemical will disappear as leaded gasoline reaches obsolescence.

The uses of ethylene dibromide as a fumigant and solvent are highly dispersive and may entail risks to workers, bystanders, and localized population segments. The chemical is a component of many commercial insecticides. While solvent applications are probably confined to the industrial environment, fumigation operations are carried out under field conditions where control may be lax or difficult. Because of its low vapor pressure. ethylene dibromide is a persistent chemical, and the fumigation of enclosed spaces may entail risks to those entering later. Control of these applications is largely dependent on personnel training and product

application data. Legislative control can be assured only through restrictions on the sale and use of the material.

There are no data available on atmospheric accumulation of ethylene dibromide. As with other chemicals, it would be valuable and interesting to balance the rate of loss to the atmosphere against the assimilative capability of the atmosphere for this chemical, but this is a formidable task. Judging from available literature, there seems a general consensus that significant accumulation of ethylene dibromide in the atmosphere is unlikely.

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